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(54) **Reduction of foreign particulate matter on semiconductor wafers.**

(57) A substantial reduction in the foreign particulate matter contamination on surfaces, such as the surfaces of semiconductor wafers, is achieved by treating the surfaces with a solution comprising a strong acid and a very small amount of a fluorine-containing compound. A preferred method employs a solution containing sulfuric acid, hydrogen peroxide and a very small amount of hydrofluoric acid, which is effective in reducing foreign particulate matter contamination, without significant etching, of the surface being treated.

EP 0 477 504 A1

This invention relates to the cleaning of surfaces, and, more particularly, to an improved method of reducing foreign particulate matter on surfaces of semiconductor wafers.

In the manufacture of semiconductor devices, cleaning steps are performed before or after various steps to remove foreign contaminants or impurities from the surfaces of semiconductor wafers. For example, wafers are commonly polished with abrasive slurries to produce smooth, polished surfaces; after polishing, it is necessary to remove the slurry and other surface contaminants from the wafers. Removal of foreign particulate matter, such as metallics and organic contaminants, is also required prior to high temperature processing steps, such as diffusion, thermal oxidation and epitaxial growth; otherwise, these impurities can adversely affect surface stability, reliability, electrical performance and production yield of devices. Cleaning steps are also commonly carried out after stripping photoresist materials from the surfaces of wafers and following etching steps.

Various techniques are used to clean foreign particulate matter from the surfaces of semiconductor wafers, such as chemical removal, centrifugation, air-stream or water jet cleaning, mechanical scrubbing and so forth. One commonly used chemical cleaning solution contains sulfuric acid and hydrogen peroxide (see, for example, Kern, W., "Hydrogen Peroxide Solutions For Silicon Wafer Cleaning", RCA Engineer, 28-4 (Jul./Aug. 1983), pp. 99-105), but that solution is somewhat limited in its foreign particulate matter removal effectiveness. Other methods employing various cleaning solutions are exemplified by the disclosures in the following: US-A-4 261 791, US-A-4 711 256 and US-A-4 828 751.

Now, an improved method has been discovered for reducing foreign particulate matter on a surface, particularly a surface of a semiconductor wafer. In accordance with the invention, the surface to be treated is contacted with a solution comprising a strong acid and a very small amount of a fluorine-containing compound, which is effective in reducing foreign particulate matter contamination, without significant etching, of the surface. In a preferred method, there is employed a solution which further contains an oxidizing agent, such as hydrogen peroxide, and in which the fluorine-containing compound is hydrofluoric acid.

In the practice of the invention, a substantial reduction, e.g. an order of magnitude or greater, in the foreign particulate matter concentration on the surface being treated has been achieved.

It should be noted that various etching solutions are known which contain hydrofluoric acid, such as those disclosed in GB-A-989 025 and US-A-4 100 014. See also US-A-2 809 103; US-A-4 220 706, US-A-4 681 657 and US-A-4 705 760. Surprisingly, however, in view of these disclosures, it has now been found, that a substantial improvement in reducing foreign particulate matter concentration can be effected without significant etching of the surface being treated. The reduction occurs as a result of removing foreign particulate matter from the surface and repelling further contamination of the surface from the solution itself.

As discussed above, the solution employed according to the invention, comprises a strong acid and a very small amount of a fluorine-containing compound. Any suitable strong acid can be employed, such as sulfuric acid, nitric acid and trifluoroacetic acid, although sulfuric acid is preferred. A particularly preferred fluorine-containing compound is hydrofluoric acid.

In carrying out the method, a very small amount of the fluorine-containing compound is employed. This amount is effective in reducing foreign particulate matter contamination of the surface being treated, but without significant etching of the surface. Without being bound by theory, it is believed that this is accomplished by establishing a chemophobic surface upon contacting the surface with the solution, in contrast with a chemophilic surface.

Generally speaking, when a wafer surface is contacted with a conventional cleaning solution, a chemophilic surface is formed, with a residual film of the solution remaining on the surface. Foreign particulate matter from the solution is essentially trapped by the residual film on the surface being cleaned. These particulate contaminants once on the surface resist removal with cleaning solutions ordinarily employed by those skilled in the art. It is believed, however, that the method of the invention provides a chemophobic condition on the surface, where no observable residual film of the solution remains, although tiny droplets may still be present. With this condition, the solution and particulate contaminants are allowed to drain, thus producing a haze-free surface.

It is important to note, however, that although the fluorine-containing compound is employed in an amount which is sufficient to establish a chemophobic surface, it does not cause etching of the surface to a significant extent. In general, the amount is such that the surface being treated is etched at a rate of less than about 2 nm/min., preferably less than about 0.5 nm/min., and most preferably less than about 0.2 nm/min.

In general, the exact amount of the fluorine-containing compound that is employed will depend upon the nature of the compound, the temperature of the solution, the contacting time, etc. However, for hydrofluoric acid, the amount will usually range up to about 2.5×10^{-3} percent by weight, and more preferably up to

about 2×10^{-4} percent by weight, based on the weight of the solution.

Various other ingredients may be added to the solution. For example, a suitable oxidizing agent, such as hydrogen peroxide or nitric acid, may be added to further enhance the cleaning rate of the solution, with hydrogen peroxide being preferred. The amount of oxidizing agent employed may vary widely, but it typically ranges from about 5 to about 25 percent, based on the weight of the strong acid in the solution. Other ingredients may be added, depending on the nature of the surface being treated, as well as the nature of the particulate matter. For example, phosphoric acid may be added if particles of silicon nitride are being removed from the surface, as well as standard ingredients such as surfactants.

In carrying out the method of the invention, the wafers are preferably immersed in the solution. Generally, this is performed at a temperature ranging from ambient to about 150°C, and preferably from about 90° to about 115°C, and for a period of time ranging from about a few seconds to about 10 minutes. The actual temperature and time will vary, however, depending on a number of factors, such as the exact formulation of the solution, the nature of the surface being treated and of the particulate matter being removed, and so forth, as will be apparent to those skilled in the art.

Generally, the wafers are then rinsed, preferably with deionized water. Typically, this is performed in two steps, first with hot deionized water, such as at a temperature ranging from about 30° to about 90°C, preferably from about 40° to about 50°C, for about 1 to about 10 minutes, followed by a final rinse, at a temperature ranging from about 20°C to about 25°C for about 1 to about 10 minutes. Then, the wafers are usually subjected to a drying step, such as in a centrifuge.

In addition, it should be noted that besides treating silicon-containing surfaces, such as silicon and silicon oxide, the method of the invention can be effectively used in treating a wide variety of surfaces of other substrates, such as oxides, metals, glasses, etc.

The following examples are provided to illustrate the invention.

EXAMPLES 1-12

Oxide coated silicon wafers (Examples 1-6) or bare silicon monitor wafers (Examples 7-12) were contacted with solutions, containing sulfuric acid, hydrogen peroxide and varying amounts of hydrofluoric acid, as outlined in TABLE I below. The procedure involved first immersing the wafers in the solutions at 100°C for 10 minutes. After that, the wafers were rinsed with deionized water at 45°C for 5 minutes. This was followed by another rinse, again with deionized water, but at a temperature of 22°C for 5 minutes. The wafers were then spun dry for 4 minutes in hot flowing air. In each case, it was found that the oxide etch rate was less than 0.2 nm/min., and a hydrophobic surface was established, with no noticeable surface haze after 7 days. The results of these tests are summarized in TABLE II below.

TABLE I

Wafer Group and Example No.	Ingredient (% by Wt.)		
	H ₂ SO ₄	H ₂ O ₂	HF
1	88.9	11.1	1.3×10^{-4}
2	88.9	11.1	6.5×10^{-5}
3	88.9	11.1	1.3×10^{-5}
4	88.9	11.1	6.5×10^{-6}
5	88.9	11.1	1.3×10^{-6}
6	88.9	11.1	Trace
7	88.9	11.1	Trace
8	88.9	11.1	1.3×10^{-6}
9	88.9	11.1	6.5×10^{-6}
10	88.9	11.1	1.3×10^{-5}
11	88.9	11.1	6.5×10^{-5}
12	88.9	11.1	1.3×10^{-4}

TABLE II

Wafer Group and Example No.	Oxide Etch Rate ¹ (nm./min.)	Surface Characteristics (Chemophobic vs. Chemophilic)	Surface Haze (After 7 days)
1	0.135	Chemophobic	No
2	0.055	Chemophobic	No
3	0.005	Chemophobic	No
4	0	Chemophobic	No
5	-0.005	Chemophobic	No
6	-0.005	Slightly Chemophobic	No
7	-0.036	Slightly Chemophobic	No
8	-0.034	Chemophobic	No
9	-0.032	Chemophobic	No
10	-0.032	Chemophobic	No
11	-0.031	Chemophobic	No
12	-0.036	Chemophobic	No

¹ (A negative number indicates oxide growth rate).

EXAMPLE 13 AND COMPARATIVE

EXAMPLES A AND B

In each of these examples, the procedure of Example 1 was followed, except that the wafers were bare silicon monitor wafers, and after the wafers were spun dry, a 400 nm thick layer of polysilicon was deposited by standard CVD techniques. In Example 13, the solution contained sulfuric acid, hydrogen peroxide and hydrofluoric acid, while in Comparative Examples A and B, the solutions contained sulfuric acid and hydrogen peroxide, but no hydrofluoric acid was added. The compositions of the solutions are outlined in TABLE III below.

Particle counts were then determined, by employing a TENCOR Model 4000 or Model 5500 measurement tool (commercially available from Tencor Instruments, Mountain View, California). The resulting particle counts are summarized in TABLE IV below. It should be noted that the numerical result indicates the number of particles on the wafer having a size of 0.7 or 1.2 μ , respectively, or larger, measured in cross-sectional area. As shown in TABLE IV, the use of the solution of Example 13 showed a substantial reduction in foreign particulate matter concentration, as compared with the use of the standard H_2SO_4/H_2O_2 cleaning solution. In addition, the wafer treated with the solution in Example 13 did not show a noticeable haze after 90 days, while the wafers treated with the solutions in Comparative Examples A and B did show a noticeable haze after only 2 days.

TABLE III

Example or Comparative Example No.	Ingredient (% by Weight)		
	H_2SO_4	H_2O_2	HF
13	88.9	11.1	6.5×10^{-5}
A	88.9	11.1	0
B	88.9	11.1	0

TABLE IV

Example Or Comparative Example No.	Particulate Matter Concentration		Surface Haze (After 2 Days)
	1.2 u	0.7 u	
13	3	14	No
A	29	408	Yes
B	14	393	Yes

EXAMPLES 14 AND 15 AND COMPARATIVE

EXAMPLES C AND D

In each of these examples, the procedure of Example 1 was followed, except that the wafers were bare silicon monitor wafers, and after the wafers were spun dry, a 400 nm thick layer of polysilicon was deposited by standard CVD techniques. In Examples 14 and 15, the solution contained sulfuric acid, hydrogen peroxide and hydrofluoric acid, while in Comparative Examples C and D, the solutions contained sulfuric acid and hydrogen peroxide, but no hydrofluoric acid was added. The compositions of the solutions are outlined in TABLE V below.

Particle counts were then determined, by employing a TENCOR Model 4000 or Model 5500 measurement tool (commercially available from Tencor Instruments, Mountain View, California). The resulting particle counts are summarized in TABLE VI below. It should be noted that the numerical result indicates the number of particles on the wafer having a size of 0.7 or 1.2 μ , respectively, or larger, measured in cross-sectional area. As shown in TABLE VI, the use of the solutions of Examples 14 and 15 showed a substantial reduction in foreign particulate matter concentration, as compared with the use of the standard $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ cleaning solution. In addition, the wafers treated with the solutions in Examples 14 and 15 did not show a noticeable haze after 90 days, while the wafers treated with the solutions in Comparative Examples C and D did show a noticeable haze after only 2 days.

TABLE V

Example or Comparative Example No.	Ingredient (% by Weight)		
	H_2SO_4	H_2O_2	HF
14	88.9	11.1	6.5×10^{-5}
15	88.9	11.1	6.5×10^{-5}
C	88.9	11.1	0
D	88.9	11.1	0

TABLE VI

Example Or Comparative Example No.	Particulate Matter Concentration		Surface Haze (After 2 Days)
	1.2 u	0.7 u	
14	10	106	No
15	7	72	No
C	2,998	12,075	Yes
D	740	32,000 +	Yes

Claims

1. A method of treating a surface, which comprises contacting said surface with a solution comprising a strong acid and a very small amount of a fluorine-containing compound, which is effective in reducing foreign particulate matter contamination, without significant etching, of said surface.
2. The method of claim 1, wherein said amount of said fluorine-containing compound is sufficient to establish a chemophobic surface, without significant etching of said surface being treated.
3. The method of claim 1 or 2, wherein said fluorine-containing compound comprises hydrofluoric acid.
4. The method of any of the preceding claims 1 to 3, wherein said solution contains hydrofluoric acid in an amount of up to about 2.5×10^{-3} percent by weight and preferably in an amount of up to about 2×10^{-4} percent by weight.
5. The method of any of the preceding claims 1 to 4, wherein said strong acid is selected from the group consisting of sulfuric acid, nitric acid and trifluoroacetic acid.
6. The method of any of the preceding claims 1 to 5, wherein said surface is etched at a rate of less than about 0.5 nm/min and preferably at a rate of less than about 0.2 nm/min.
7. The method of any of the preceding claims 1 to 6, wherein said surface is contacted with said solution for a period of time ranging from about a few seconds to about 10 minutes, and wherein said solution is maintained at a temperature ranging from about 90° to about 115°C.
8. The method of any of the preceding claims 1 to 7, wherein said solution further comprises an oxidizing agent.
9. The method of claim 8, wherein said oxidizing agent comprises hydrogen peroxide.
10. The method of any of the preceding claims 1 to 9, wherein said surface is the surface of a semiconductor wafer.



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EUROPEAN SEARCH REPORT

Application Number

EP 91 11 2984

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y,A	International Electron Devices Meeting 1988, 11-14 December, San Francisco December 1988, pages 726 - 729; A. OHSAWA ET AL: "Improvements of trench capacitor characteristics by pre-oxidation surface cleaning with a HNO3-HF-H2O solution" * page 726 EP 91112984030 * - - -	1-3,5,6, 10,8,9,	H 01 L 21/306
Y	JOURNAL OF THE ELECTROCHEMICAL SOCIETY. vol. 136, no. 11, November 1989, MANCHESTER, NEW HAMP pages 3459 - 3462; T. SHIBATA ET AL: "Si surface cleaning and epitaxial growth of GaAs on Si by electron cyclotron resonance plasma-excited M-B-E at low temperatures" * page 3459, right-hand column * - - -	8,9	
D,A	US-A-4 261 791 (S. SHWARTZMANN) * claim 1 * - - -	1	
D,A	US-A-4 220 706 (M. A. SPAK) * abstract * - - -	1,3,5,10	
A	JOURNAL OF THE ELECTROCHEMICAL SOCIETY. vol. 136, no. 1, January 1989, MANCHESTER, NEW HAMP pages 175 - 182; G. J. VALCO ET AL: "Plasma deposited silicon nitride for indium phosphide encapsulation" * page 175, right-hand column * - - - - -	8,9	TECHNICAL FIELDS SEARCHED (Int. Cl.5) H 01 L
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
Berlin		07 January 92	ROUSSEL A T
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